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## Bifunctional covalent organic frameworks with two dimensional organocatalytic micropores†

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We report the successful incorporation of bifunctional (acid/base) catalytic sites in the crystalline organocatalytic porous COF (2,3-DhaTph). Due to the presence of acidic (catachol) and basic (porphyrin) sites, 2,3-DhaTph shows significant selectivity, reusability, and excellent ability to perform the cascade reaction.

Covalent organic frameworks (COFs)<sup>1</sup> are a new class of crystalline porous materials constructed from light elements like H, B, C, N, O, Si, etc.<sup>2</sup> Although research on these materials received immense attention due to their potential applications in gas adsorption, charge carrier transport, and optoelectronics,<sup>3</sup> these porous materials are less explored as catalysts owing to their limited stability in aqueous, acidic and alkaline media.<sup>4</sup> In principle, COFs can be used as catalysts mainly in two ways: (1) as a support for catalytically active nanoparticles,<sup>5</sup> and (2) direct organocatalysis using catalytically active organic building units within the COF.<sup>6</sup> Among these catalytic applications, heterogenous organocatalytic COFs are more promising, because they have a large scope in pharmaceutical and food industries.<sup>7</sup> Here, we report the successful synthesis of a bifunctional catachol-porphyrin COF, consisting of both acidic and basic sites, which can act as a heterogeneous catalyst for one pot deprotection of acetal groups followed by Knoevenagel condensation reaction.8 Even though there has been a report of a porphyrin COF ( $[Pyr]_r$ -H<sub>2</sub>P-COF) used as an organocatalyst,<sup>6b</sup> the incorporation of the bifunctionality in the COF backbone for catalysis is still unprecedented.

Bifunctional heterogeneous catalysts are more preferred for cascade/tandem/one-pot synthesis reactions, because of the fixed location of the acidic and basic sites, within the framework. Also the large surface area, chemical stability and ordered crystalline structure with separated antagonist sites are the essential requirements of a heterogeneous bifunctional catalyst to achieve the highest catalytic activity. The large surface area will provide greater exposure of the catalytic sites to the incoming reactants. The chemical stability will help to avoid the contamination due to catalyst degradation, whereas high crystallinity will provide information on the structure and the exact position as well as the distance between the antagonist catalytic sites. Although a few polymer based organocatalysts are reported in the literature for the cascade reaction, due to the amorphous nature of the catalysts, the exact position of the antagonist catalytic sites and the spatial separation between them were very poorly understood.8 Moreover, the reported post functionalization strategy does not ensure 100% incorporation of the catalytic sites in the framework.<sup>6b,9</sup> Thus, the synthesis of bifunctional heterogeneous catalysts having high crystallinity, porosity and chemical stability is still a challenging task.<sup>10</sup> The COFs reported in this paper, 2,3-DhaTph and 2,3-DmaTph, were synthesized by reversible Schiff-base reaction using 2,3-dihydroxyterephthalaldehyde (2,3-Dha)/2,3-dimethoxyterephthalaldehyde (2,3-Dma) and a 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphine unit (Tph) in dichlorobenzene (o-DCB,) and dimethylacetamide (DMAc) with a catalytic amount of 6.0 M acetic acid (Fig. 1) (ESI,† Section 2). The PXRD patterns of the as-synthesized COFs showed good crystallinity with a highly intense peak at  $\sim 3.6^{\circ} 2\theta$  corresponding to the [100] plane reflections and low intense peaks at  $\sim$  7.3° and ~19–25° 2 $\theta$ , which were assigned to [200] and [001] facets (d spacing = 4.0 Å). The diffraction patterns of the synthesized COFs are similar to that of eclipsed stacking model of the COF structures built using the SCC-DFTB method (Fig. 2a, S4, ESI†).<sup>11</sup> From the Pawley refinement, we could conclude that the unit cell values for **2,3-DhaTph** are a = 24.7, b = 24.6, c = 4.0 Å;  $\alpha = 92.9$ ,  $\beta =$ 90.2,  $\gamma = 92.7$ ; *P*1 space group; and for **2,3-DmaTph** are *a* = 25.2, b = 24.6, c = 4.1 Å;  $\alpha = 90.1, \beta = 89.7, \gamma = 88.4; P1$  space group (Section S3, ESI<sup>+</sup>). The crystal structure analysis of the monomers of 2,3-DhaTph and 2,3-DmaTph indicated that these COFs exist only in the enol-imine form (Fig. 1 and Fig. S11, ESI†).

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Fig. 1 The synthesis of 2,3-DhaTph and 2,3-DmaTph by the condensation of Tph and 2,3-Dha/2,3-Dma. The catalytically active porphyrin and catecholic –OH groups are shown in coral and cyan colors, respectively. An ORTEP diagram of 2,3-DhaTph and 2,3-DmaTph monomer units.



Fig. 2 (a) The PXRD pattern of **2,3-DhaTph** compared with simulated eclipsed and staggered. (b and c) Stacking diagram and the eclipsed stacking model of **2,3-DhaTph**. (d) Staggered stacking model of **2,3-DhaTph**. (e) PXRD pattern of **2,3-DmaTph** compared with simulated eclipsed and staggered. (f and g) Stacking diagram and the eclipsed stacking model of **2,3-DmaTph**. (h) Staggered stacking model of **2,3-DmaTph**.

The presence of *trans* conformation of imine bonds and the presence of intramolecular hydrogen bonding [ $-O-H \cdots N = C$ ; D = 2.579 (2), d = 1.858 (2) Å, and  $\theta = 146.1^{\circ}$  (3)] in **2,3-DhaTph** have been confirmed from the monomer crystal structure, which leads to the rigid structure enhancing the crystallinity (Fig. 1).<sup>10b,12</sup> As a result, the PXRD pattern of **2,3-DhaTph** is much more intense than that of **2,3-DmaTph**, since the intramolecular H-bonding is absent in **2,3-DmaTph** (Fig. 1). The appearance of a strong characteristic imine -C—N stretching frequency in the FT-IR spectrum at 1612 cm<sup>-1</sup> for **2,3-DhaTph** (Fig. S5, ESI†) and 1608 cm<sup>-1</sup> for **2,3-DmaTph** (Fig. S6, ESI†) confirmed the formation of COFs. Also, the disappearance of the stretching frequency of the -C—O group (1661 of **2,3-Dha** and 1676 cm<sup>-1</sup> of **2,3-Dma**) and the  $-NH_2$  group (3100–3400 cm<sup>-1</sup>) of **Tph** in the

FT-IR spectra of **2,3-DhaTph** and **2,3-DmaTph** confirmed the formation of imine -C—N bonds. The solid state <sup>13</sup>C CP-MAS NMR spectrum confirmed the formation of imine -C—N bonds, as it shows the characteristic signals at  $\delta$  160.8 (Fig. S7, ESI†) and 154.2 (Fig. S8, ESI†) ppm respectively. These chemical shifts of imine -C—N appear closer to the monomer unit values of **2,3-DhaTph** ( $\delta$  161.3) (Fig. S10, ESI†) and **2,3-DmaTph** ( $\delta$  154.9) (Fig. S12, ESI†). The morphological analysis of **2,3-DhaTph** and **2,3-DmaTph** done using SEM and TEM imaging indicates that **2,3-DhaTph** is composed of 100–200 nm thin platelet like morphology, whereas **2,3-DmaTph** consists of 30–50 nm average sized sheet like morphology (Section S10, ESI†).

The thermal stability of the activated COFs was confirmed by TGA analysis, which showed high thermal stability up to 300  $^\circ \rm C$ 



Fig. 3 (a) N<sub>2</sub> adsorption isotherms of **2,3-DhaTph** and **2,3-DmaTph**. (b) Comparative TEM images, as synthesized and after 3rd cycle of **2,3-DhaTph** and **2,3-DmaTph**. (c) The catalytic activity towards acid-base catalyzed reaction with various reactants. (d) Kinetics of the cascade reaction between **1** and malononitrile. (e) Comparison of the recyclability studies performed for **2,3-DhaTph** and **2,3-DmaTph**.

(Section S9, ESI<sup>+</sup>). The N<sub>2</sub> adsorption isotherms collected at 77 K for the activated COFs showcase a typical Type-IV isotherm (Fig. 3a) with the Brunauer-Emmett-Teller (BET) surface area of 1019 and 668 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. S14 and S17, ESI<sup> $\dagger$ </sup>). The pore width values calculated using the NLDFT method were found to be 2.2 and 1.4 nm which are in close agreement with the theoretically predicted pore width (Fig. 1). The surface area and pore size of 2,3-DmaTph are lower than that of 2,3-DhaTph, which is well justified as twisted conformation of phenyl rings in the former case shows disturbed stacking of 2D layers, which finally reduces the crystallinity as well as porosity. We have analyzed the chemical stability of these COFs in aqueous, acidic (3N HCl) and alkaline (3N NaOH) media. Both COFs showed good aqueous stability for more than 7 days, which was confirmed by PXRD, FT-IR and porosity studies. The presence of -OH and -OCH<sub>3</sub> groups adjacent to the imine bonds in these COFs probably helped to improve the hydrolytic stability. Similarly, the stability of these COFs in 3N HCl was further confirmed by FT-IR, PXRD and SEM studies (Section S12, ESI<sup>†</sup>).<sup>10</sup> 2,3-DhaTph showed higher structural integrity than 2,3-DmaTph, probably due to the strong intramolecular hydrogen bonding  $[-O-H \cdots N = C]^{10b,12}$  Due to the protonation of the inner porphyrin core by an acid a decrease in the surface area has been observed (before 1019, after 652  $m^2 g^{-1}$  for 2,3-DhaTph and before 668, after 307 m<sup>2</sup> g<sup>-1</sup> for 2,3-DmaTph).<sup>10b</sup> Both 2,3-DhaTph and 2,3-DmaTph are unstable in basic medium (3N NaOH).

The **2,3-DhaTph** COF possesses separate antagonist catalytic sites in which catecholic –OH groups act as weak acidic sites,<sup>13</sup> whereas porphyrin units and imine bonds act as basic sites, with high chemical stability in aqueous/acidic media along with high crystallinity and porosity. Hence, we have decided to explore the catalytic activity of this COF for the acid–base catalyzed one-pot cascade reactions.<sup>8</sup> The catalytic activity of

**2,3-DhaTph** was analyzed in the presence of 10 mg of the COF catalyst using a model reaction (Fig. 3c), wherein benzaldehydedimethylacetal (**1a**) (152 mg, 0.1 mmol) reacts with malononitrile (72.6 mg, 0.11 mmol) in toluene (1.5 mL) and water (0.5 mL) at 80 °C. In the case of **2,3-DhaTph** the formation of the desired product 2-benzylidenemalononitrile (**3a**) with excellent isolated yield (96%) was observed. The detailed kinetic study showed that the completion of reaction occurs within 90 min (Fig. 3d). It was understood from the control experiments that this cascade reaction proceeds through two sequential steps: (1) the acid catalyzed deacetalization of benzaldehydedimethylacetal (**1a**) to yield benzaldehyde (**2a**); and (2) the base catalyzed Knoevenagel condensation reaction to yield 2-benzylidenemalononitrile (**3a**). (Fig. 3c and Section S13, ESI†).

In order to analyze the necessity of the catalyst for the cascade reaction, a model reaction was performed without the addition of the catalyst. The reactions without a catalyst yielded only 5% of product **3a** during the estimated time span of 90 min.

The reaction performed without a catalyst (blank) (Section S13, ESI<sup>†</sup> Table 3, entry 1) under the same conditions yielded only 25% of intermediate **2a**, probably due to the deacetalization of **1a** by water, which has been used as a solvent. We have explored the substrate scope of the **2,3-DhaTph** catalyst using a number of substituted dimethyl acetal reactants, keeping all other reaction conditions the same. In general, excellent conversions (>80%) to the desired products were observed (Section S13, ESI,<sup>†</sup> Table 4, entries 2–5); despite the presence of an electron donating (-Me and -OMe) or withdrawing group (-NO<sub>2</sub>) on the acetal based reactants. As shown in Fig. 3c, the reactant size (molecular dimensions) did not affect the reactivity of the starting materials, which emphasizes the utility of **2,3-DhaTph** for the broad spectrum of the catalytic reactions.

The kinetics of the cascade reaction after the addition of the catalyst shows that as the rate of the reaction increases with time the amount of reactant 1a starts decreasing along with a related increase in the corresponding product 3a. As shown in Fig. 2d, with increasing time, the formation of 3a steadily increases up to 60 min yielding  $\sim$  90% product for the 2,3-DhaTph catalyst. The probable reason for the significant activity shown by the 2.3-DhaTph catalyst may be the fine distribution of acidic and basic sites in the crystalline COF and periodic arrangement of these centres distributed over the entire COF matrix. In order to prove the necessity of acidic and basic sites for catalyzing the cascade reaction,<sup>14</sup> we have repeated the same catalytic reaction in the presence of 2,3-DmaTph as a catalyst, which holds only basic porphyrin centers but lacks acidic catecholic -OH functionality, which has been replaced by -OMe functionality. In this case, the reaction proceeds very slowly giving only 52% yield of 3a in 90 min (Section S13, ESI,† Table 3); as shown in Fig. 3d. Hence, it is clear that only basic sites are not sufficient to catalyze the cascade reaction (Fig. 3). The solid catalysts can be recycled for more than five times without loss in product yield as shown in Fig. 3e. 2,3-DhaTph has showed excellent recyclability for more than five catalytic cycles giving yields over  $\sim$  81% in an estimated time span of 90 min. In the case of 2,3-DmaTph, as expected, we have also observed the recyclability up to 5 cycles, but very limited yield up to  $\sim$  42% (Fig. 3d and e and Section S13, ESI<sup>†</sup>).

In conclusion, we have synthesized a catalytically active COF **2,3-DhaTph** with weak acidic and basic sites for catalyzing the cascade reaction. **2,3-DhaTph** showed a large surface area, high crystallinity as well as porosity than **2,3-DmaTph**, which lacks intramolecular hydrogen bonding within the framework. The potential of **2,3-DhaTph** for catalyzing the cascade reaction is validated by the good catalytic activity shown towards the cascade reaction with very high product yield and recyclability over 5 cycles. The necessity of the basic and acidic sites in a catalyst for catalyzing the cascade reaction has been further validated by utilization of methoxy functionalized **2,3-DmaTph**.

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- 14 The concept of necessity of both acidic (quinolic–OH) and basic (porphyrin) groups for catalyzing the aforementioned catalytic reaction was confirmed by using a literature reported **DhaTph** catalyst, which has both acidic as well as basic centers, with similar stability.<sup>10b</sup> Also, in the case of **DhaTph**, we have observed a similar yield of ~94% of product **3a** (ESI,† Section S13).